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ON THE RAMAN AND INFRARED SPECTRA OF BENZYL ACETATE

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ABSTRACT. The Raman spectrum of benzyl acetate in the liquid state and the infrared absorption bands of the pure liquid and its solutions in CCl_4 and $HCCl_3$ have been investigated A reasonably complete vibrational assignment of the observed frequencies of the molecule of benzyl acetate has been made by treating the vibrations of the phenyl group and the $-CH_2OCOCH_3$ group independently.

INTRODUCTION

A large amount of work on the assignment of modes of vibration to various vibrational frequencies in the molecules of benzene and its derivatives have already been carried out (Pitzer and Scott, 1943, Sponer and Kirby-Smith, 1941, Mecke-Kerkhof, 1951; Whiffen, 1956, Stephenson *et al*, 1961, Sirkar *et al*, 1964 and others). In most cases the substituent is either a single atom or a single group containing a small number of atoms However, if the substituent group contains larger number of atoms the Raman and infrared spectra of the compound become more complex and in such cases very little work on the enumeration of the vibrational modes in the molecules seems to have been done

A systematic programme has been undertaken so that a reasonably complete vibrational assignment of the frequencies of vibrations of molecules of substituted benzene compounds with large substituent groups may be made and in this paper the results obtained with benzyl acetate have been presented

An incomplete study of the Raman spectrum of this compound was made by Morris (1931) while the infrared absorption bands due to this compound were reported by Lenormant (1948) The Raman and infrared spectra of the compound have been re-investigated in order that as many vibrational frequencies as possible are obtained

EXPERIMENTAL

The sample of benzyl acetate supplied by Société des Usines Chimiques, France, was first fractionated and the proper fraction was distilled several times under reduced pressure before use. The Raman spectrum of the liquid was investigated in the usual manner and the states of polarisation of some of the Raman

lines were determined qualitatively from the ratio of the intensities of the horizontal and vertical components photographed simultaneously with the double image prism. The Fuess glass spectrograph used has a dispersion of about 13 Å/mm and 19 Å/mm in the Hg 4047 Å and 4358 Å regions respectively. The infrared spectra of the compound in dilute solutions in CCl_4 and $HCCl_3$ and also of a thin film of the pure liquid were recorded on a Perkin-Elmer Model 21 double beam infrared spectrophotometer with NaCl optics The absorption due to the pure liquid in a 0 025 mm thick cell was investigated carefully so that the existence of very weak bands which might have escaped observation with the dilute solutions and the thin film of pure liquid, could be ascertained The spectrophotometer was calibrated with the standard absorption bands of atmospheric water vapour carbon, dioxide and of a polystyrene film

RESULTS AND DISCUSSION

The frequency-shifts of the Raman lines (in cm^{-1}) of benzyl acetate together with the estimated relative intensities are given in Table I. The states of polarisation of the lines are denoted by the letters *P* and *D* as usual The table also contains the wave numbers (cm^{-1}) of the infrared bands due to the pure liquid and its solutions in CCl_4 and $HCCl_3$ The intensities and the nature of the bands are listed as *s*—strong; *m* medium, *w*—weak; *b*—broad; *sh*—shoulder and *v*—very A probable assignment of the various vibrational frequencies is given in the last column of Table I

The molecule of benzyl acetate contains 21 atoms which give rise to 57modes of vibration Since the molecule contains no other symmetry element than the element of identity all these would give rise to 57 frequencies of vibration, all allowed in both the Raman scattering and infrared absorption

In order to be able to assign the modes of vibration arising from the phenyl group in the molecule of benzyl acetate the observed Raman shifts and infrared absorption frequencies of the compound have been compared with the Raman shifts of a number of benzyl derivatives reported earlier by Reitz and Stockmair (1935). From this comparison it is easily found that the frequencies of certain Raman lines characteristic of the vibration of the phenyl ring vary only slightly from one benzyl compound to another This indicates that so far as the phenyl group is concerned, the modes of vibration and their frequencies are not sensitive to the variation in the nature of the atoms or group of atoms (denoted by *X*) in the substituent $-CH_2X$ This simplifies the enumeration of the vibrational modes of the benzyl acetate molecule to the extent that the vibrations arising from the phenyl group and the $-CH_2OCOCH_3$ group may be treated separately.

a) *Assignments of the vibrations of the phenyl group*

If the whole of the $-CH_2OCOCH_3$ group is treated as a single mass point the molecule of benzyl acetate would have to a first approximation, the symmetry

of the point group C_{2v}. Under this symmetry, the classwise breaking up of the 30 vibrational modes of the monosubstituted benzene compound and the classification of the states of polarisation of the Raman lines arising from the in-plane vibrational modes are well known. The experimentally observed states of the polarisation of some of the easily recognisable Raman lines of benzyl acetate justify the correctness of the assumption.

TABLE I

Benzyl acetate

Raman shift $\Delta\nu$cm^{-1} liquid	Infrared frequencies (cm^{-1}) Pure liquid Thin film	Pure liquid 0·025 mm cell*	Solutions in* CCl_4	Solutions in* $HCCl_3$	Corresponding modes in benzene
178 (5) D					10B
251 (1)					16B
367 (0)					17B
400 ?					16A
482 (1)					6A
559 ?					5
620 (5) D					6B
640 (2)	640 v w.	640 m			bending of O—C=O
692 (0, b)	695 s		692 s	695 s	18B
745 (0, b)	740 s				12
825 (3, b)		824 s			10A, stretching of C–CH bond
	830 m				
	900 w		897 w		
908 (0 b)	915 w		912 w		17A
	960 m		960 m	960 w	?
1002 (10)P	1000 m sh		1000 m sh	1002 m sh	1
1027 (5) P	1025 s		1022 s	1023 m sh	18A
	1040 m sh	1040 s sh		1040 m sh	15
1165 (3)	1060 w sh	1060 s.sh			9A
1175 (3)	1180 m sh	1180 s sh			9B
1214 (5) P					7A
	1230 vs.b		1227 vs	1227 vs	C—O stretch
	1260 m.sh		1250 s sh	1250 s sh	14 ?
	1362 s		1360 s	1360 m	δ (CH)$_s$ in CH_2
1375 (3, vb)					
	1380 s		1380 s	1380 m	δ (CH)$_s$ in CH_3
	1440 m.sh		1437 m sh		δ (CH)$_a$ in CH_2
1445 (2 vb)D					
	1457 s		1455 m sh		δ (CH)$_a$ in CH_3
	1485 w sh				19A
	1499 m		1495 m	1495 w	19 B
1590 (1)	1590 vw	1590 m			8A
1605 (5)D	1605 m	1605 m			8B
1735 (2, b)	1730 vs		1728 vs	1725 vs	C—O stretch
	2850 w sh				CH sym stretch in CH_3 ?
	2890 m.sh	2900 m sh			
2935 (5) P					CH sym stretch in CH_2
	2965 m	2965 s			CH asym stretch in CH_2
					CH asym stretch in CH_3
	3012 m.sh	3010 s.sh	3015 m	3010	CH asym stretch in CH_3
3037 (8)					2
	3045 m	3044 s	3045 w.sh		13
3060 (6) D	3067 m sh	3067 s.sh	3070 s.sh	3072 w sh	7B
		3080 s.sh		3085 w.sh	20 B

*only prominent bands are tabulated.

The proposed assignments of the vibrational frequencies have been based on the considerations of the intensity and character of polarisation of the Raman lines, the intensity of the corresponding infrared bands, the frequencies of vibration in other benzyl compounds and the assignments made in the case of monosubstituted benzenes.

1) *Modes almost unaffected by substitution* :

It is seen from the diagram of the normal modes of benzene (Pitzer and Scott, 1943) that in the case of monosubstituted benzenes the frequencies of vibration of the modes 6B, 7B, 9A 10A, 16A, 17A and 20B will not be affected by the substitution Also the modes 8A, 8B, 9B, 18A, 19A and 19B in general give rise to vibrational frequencies in monoderivatives of benzene which are almost the same as in benzene and change slightly from one compound to another These Raman lines and the infrared bands corresponding to those modes in benzyl acetate are shown in Table I The weak Raman line 400 cm^{-1} may correspond to the mode 16A while the other weak Raman line 908 cm^{-1} is assigned to the mode 17A The Raman line arising from the mode 10A may be masked by the strong and polarised Raman line 825 cm^{-1} which originates from a different vibration, discussed later The strong and polarised Raman line 1002 cm^{-1} which also appears as an infrared shoulder at 1000 cm^{-1} and corresponds to a similar Raman line in many monosubstituted benzenes, has been assigned to the mode 1 Similarly, the strong Raman line 3037 cm^{-1} and the strong infrared band 3045 cm^{-1} are believed to arise respectively from the modes 2 and 13 of benzene The ϕ infrared band 1260 cm^{-1} may originate from the mode 14. Table I contains the proposed assignments The frequencies arising from the modes 3 and 20A have not been ascertained

2) *Modes affected by substitution* :

Of the remaining eleven normal modes, the frequencies of vibrations, in case of the monoderivative of benzene, arising from the modes 6A, 7A, 10B, 11, 12, 16B, 17B and 18B of benzene would be appreciably changed, while those due to the modes 4, 5 and 15 will be affected to a lesser degree

The weak Raman line 482 cm^{-1} is easily identified as arising from the mode 6A while the strong Raman band 178 cm^{-1} is attributed to the mode 10B In toluene there are two strong and polarised Raman lines at 786 cm^{-1} and 1210 cm^{-1} respectively In the benzyl derivatives two corresponding moderately strong and polarised Raman lines in the region 740–765 cm^{-1} and 1200–1210 cm^{-1} respectively are observed Also, in benzyl acetate there is a weak Raman line 745 cm^{-1} corresponding to the very strong infrared band 740 cm^{-1} and a moderately strong and polarised Raman line at 1214 cm^{-1}. The two Raman lines most probably originate from the modes 12 and 7A respectively of benzene The strong infrared band 1230 cm^{-1} is believed to arise from other cause which has been discussed later.

The weak Raman line 692 cm^{-1} having its counterpart in the very strong infrared band 695 cm^{-1}, has been assigned to the mode 18B Since the other benzyl compounds do not show any Raman line corresponding to the Raman line 640 cm^{-1} (infrared band 640 cm^{-1}) of benzyl acetate, this line obviously does not represent a vibration of the phenyl group On consideration of intensity the very weak Raman lines 367 cm^{-1} and 254 cm^{-1} have been attributed to modes 17B and 16B respectively. Moreover, since the frequencies of the modes 15 and 5 are affected slightly on substitution, the weak infrared band 1040 cm^{-1} and the very weak Raman line 559 cm^{-1} respectively probably represent these modes Raman line due to the mode 4 has not been observed All the proposed assignments are shown in Table I.

b) *Vibrations of the CH_3COOCH_2 group* .

If the phenyl group is taken to be a single unit 27 vibrational frequencies would arise from this configuration. From the elaborate Raman and infrared data on the molecule of methyl acetate (CH_3COOCH_3) reported by Wilmshurst (1957), it is seen that many of the vibrational frequencies of this group except those arising from CH_3, CH_2 and C — O groups are so close to the frequencies of vibration of the phenyl group, that it has been possible to detect only a few of them. However, the following characteristic group vibrational frequencies are easily recognised Table I contains the proposed assignments

1) *Carbonyl frequency*

The weak and broad Raman line at 1735 cm^{-1} corresponding to the strong infrared band at 1730 cm^{-1} due to the pure liquid is easily assigned to the vibrational frequency arising from the stretching of the C = O bond

2) *CH deformation vibrations* :

The Raman spectrum of benzyl acetate shows two very broad lines at 1375 and 1445 cm^{-1} and in the infrared spectrum there are three strong bands at 1362, 1380 and 1457 cm^{-1} There will be one symmetric and one asymmetric CH deformation vibrational frequencies arising from the CH_2 group A comparison with the spectra due to the other benzyl compounds fixes these frequencies fairly reasonably at 1360 and 1440 cm^{-1} respectively. The very broad Raman line 1375 cm^{-1} may in part also correspond to the strong infrared band 1380 cm^{-1}, which is the frequency of the symmetric CH deformation in the methyl group while at least one component of the antisymmetric and doubly degenerate CH deformation in the CH_3-group is represented by the strong infrared band at 1457 cm^{-1} The Raman line corresponding to this mode may have merged in the broad Raman line 1445 cm^{-1}.

3) *C-H stretching vibrations* :

In the Raman spectrum of benzyl acetate there is a strong polarised Raman line at 2935 cm^{-1} while the infrared spectrum shows a strong band at 2965 cm^{-1}

and three medium shoulders at 2850, 2900 and 3010 cm^{-1}. From a comparison with the Raman shifts of other benzyl compounds the Raman line 2935 cm^{-1} has been assigned to the symmetric CH stretching vibration in the CH_2 group and the asymmetric component is most probably represented by the infrared band 2965 cm^{-1}. This band may also correspond to a component of the doubly degenerate asymmetric CH stretching vibration in the methyl group and the band 3010 cm^{-1} may represent the other component. The symmetric CH stretching vibration of the CH_3 group has not been detected in the Raman spectrum but may correspond to the weak infrared band 2850 cm^{-1}. All the assignments made are in accordance with those proposed by Wilmshurst (1957) in the case of methyl acetate.

Besides these characteristic group frequencies, the strong and polarised Raman line 825 cm^{-1}, having its counterpart in the strong infrared band 824 cm^{-1}, the Raman line 640 cm^{-1} corresponding to a medium infrared band 640 cm^{-1} and the very strong infrared band 1230 cm^{-1} probably originate in the vibrations in the acetate group of benzyl acetate. These bands in all probability correspond respectively to the strong and polarised Raman line 844 cm^{-1} (strong infrared band 843 cm^{-1}), the strong and polarised Raman line 640 cm^{-1} (medium infrared band 640 cm^{-1}) and the very strong infrared band 1239 cm^{-1} in the Raman and infrared spectra of methyl acetate reported by Wilmshurst (1957). Following the assignments proposed by him, in the latter case, the Raman lines and infrared bands in the acetate group have been assigned to the vibrations involving the stretching of the C—CH_3 bond, the bending of the O—C = O angle and the stretching of the C-O bond respectively.

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